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CHEMICAL ATTRIBUTION SIGNATURES OF CYANOGEN CHLORIDE FROM COMMERCIAL SOURCES

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RESEARCH AND TECHNOLOGY DIRECTORATE

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PREFACE

The work described in this report was authorized under project number 02P-0199 and Interagency Agreement number HSHQPM-12-X-00173 as part of the Department of Homeland Security Chemical Forensics Program. The work was started in September 2012 and completed in August 2013.

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This report has been approved for public release.

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- Timothy Allan, Alex Jestel, and other members of the ECBC Forensic Analytical Center for their expertise in CK analysis by gas chromatography– thermal conductivity detection.

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CHEMICAL ATTRIBUTION SIGNATURES OF CYANOGEN CHLORIDE FROM COMMERICAL SOURCES

1. INTRODUCTION

Since 2005, members of the U.S. Army Edgewood Chemical Biological Center (ECBC) Forensic Analytical Center (FAC), which is an International Organization for Standardization 17025-certified analytical laboratory, have collaborated with the ECBC Protective Equipment Team (PET) to perform purity analyses on samples from cylinders containing phosgene (CG), cyanogen chloride (CK), and hydrogen cyanide (AC). The majority of that work has been focused on CK. The PET members require certified documentation of the purity of these chemical agents for the tests they perform for their customers. During this collaboration, FAC members have analyzed over 70 CK cylinders, as well as several AC and CG cylinders, for purity. The primary analytical methods used have been gas chromatography–thermal conductivity detection (GC/TCD) and nuclear magnetic resonance (NMR) spectroscopy. In these analyses, the contaminating species have been identified wherever possible, with successful identification more common in the more recent analyses.

There are relatively few commercial sources for these gases. Since 2005, PET members have procured CK from the same three vendors, although these vendors' company names have changed over time. PET members have maintained records for the purchase of each cylinder, and this information has been cross-referenced with the data of agent analyses kept by the FAC team. The purchase records from between 2005 and 2013 and original data of agent analyses were re-examined for this study for the following purposes:

- to identify potential chemical attribution signatures (CAS) for CK,
- to determine whether any of these CAS are specific to a particular vendor, and
- to examine whether the CAS have changed for these vendors over the time frame of these analyses.

2. METHODS

No new analyses were performed for this study, which focused on re-examination and data mining of purity analysis reports from 2005 through 2013. The primary analytical methods used for these analyses were GC/TCD and carbon 13 (¹³C)-NMR spectroscopy.

2.1 Gas Chromatography–Thermal Conductivity Detection

The GC/TCD method used by the ECBC FAC team for CK analysis included a sample loop connected to the cylinder to allow sampling of the neat gas. Retention times for the impurities found in these cylinders were verified by comparison with authentic standard materials, and most were confirmed by GC mass spectrometry. Samples were analyzed in triplicate on an Agilent (Agilent Technologies, Inc., Santa Clara, CA) GC system (the model

changed over the time frame of these studies) using a DB-624 column, with air blanks used between samples.

Before the analysis was started, a CK cylinder was purged for at least 1 h with the valve opened to approximately 1–3 psi. Each CK cylinder was known to have a "plug" of CO₂ as a result of the filling process. If a cylinder had been analyzed without purging, the CO₂ would have accounted for as much as 30% of the total area of the chromatogram. In addition, based on the GC and detector systems used, it was necessary to determine the appropriate sample injection volume that would not saturate the CK peak response but would allow for the detection of impurity peaks of approximately 0.05% of the total area under the chromatographic curve. A typical GC chromatogram of CK is shown in Figure 1.



Figure 1. A typical GC chromatogram, expanded to show impurities.

2.2 Nuclear Magnetic Resonance Spectroscopy

Purity analysis by NMR spectroscopy was carried out as described by Henderson and Cullinan.* The samples were prepared in pressure- and vacuum-valve NMR tubes (Wilmad Labglass [Vineland, NJ], which were 528-PV-9 or equivalent) by immersing the stem of the NMR tube in a dry ice and acetone bath and condensing a stream of the gas from the cylinder into the tube. It was important to condense the gas using something colder than a standard ice bath because some common impurities (e.g., cyanogen [C₂N₂]) have boiling points well below 0 °C. NMR spectroscopy was carried out at a sample temperature of 10 °C (i.e., below the CK boiling point).

^{*} Henderson, T.J.; Cullinan, D.B. Purity Analysis of Hydrogen Cyanide, Cyanogen Chloride and Phosgene by Quantitative ¹³C NMR Spectroscopy. *Magn. Reson. Chem.* **2007**, *45*, 954–961.

This work was carried out on a Bruker (Bruker Corporation, Billerica, MA) NMR spectrometer (primarily an Avance DRX or Avance III 300 MHz system, although work was also carried out using an Avance DRX 500 MHz system). The primary NMR investigation performed was a ¹³C-NMR experiment with inverse-gated ¹H decoupling using a relaxation delay greater than $8 \times T_1$ to ensure quantitative response. A typical ¹³C-NMR spectrum of CK is shown in Figure 2. Although no ¹H signals were expected from a neat CK sample, ¹H-NMR spectroscopy was carried out, in the interests of identifying additional impurities. However, because CK provided no ¹H signals, any impurities detected only in the ¹H spectrum could not be quantitatively included in the purity determination.



Figure 2. ¹³C-NMR spectrum of CK. Inset shows an expanded view in which impurities are labeled.

3. **RESULTS AND DISCUSSION**

3.1 Purity Analysis

Purity analyses from 74 CK cylinders were examined in this data mining effort. These CK cylinders included 6 procured in 2005, 1 procured in 2006, 4 procured in 2008, 10 procured in 2009, 23 procured in 2010, 13 procured in 2011, 12 procured in 2012, and 5 procured in 2013. Of these, one cylinder was discarded because its vendor could not be verified. Another cylinder, purchased from Custom Gas Solutions (Durham, NC), was discarded as an anomaly because it contained over 20% CO₂, even after the purging process. The remaining 72 cylinders included 28 from HP Gas, LLC (Baytown, TX), including Stillwater Consultants (Stillwater, MN), LMTG (Roanoke, LA), and TL2 Gases (Sulphur, LA); 28 from Semiconductor Resources including Specialty Gases of America (Toledo, OH); and 16 from Custom Gas Solutions.

The three impurities commonly seen in the ¹³C-NMR spectrum were C₂N₂, carbon tetrachloride (CCl₄), and ethylene tetrachloride (C₂Cl₄). AC was only detected by ¹³C-NMR spectroscopy at one time at levels that were strong enough to quantify. In two other cylinders, AC was seen in the ¹³C-NMR spectrum, but it was not a strong enough signal to be reliably integrated. In the GC chromatogram, the impurities commonly identified were nitrogen and oxygen (i.e., common air components that could not be separated by the GC technique), carbon dioxide (CO₂), water (H₂O), C₂N₂, CCl₄, and AC.

Complete listings of the impurities detected in the CK purity analyses by each technique, as well as the percent concentration of each, are listed in the appendixes of this report. Appendix A lists the data analyses in reverse chronological order of when they were initially analyzed. In Appendixes B–D, that list is broken down by vendor; the data analyses are listed in reverse chronological order within each vendor group.

3.2 Attribution Signatures

Three trends were noticed in the data analyses, which may indicate patterns usable for attribution purposes (i.e., each of these were trends and not clear indicators):

- CCl₄ detection,
- CCl₄ concentration, and
- H₂O and AC by ¹H NMR

3.2.1 Carbon Tetrachloride Identification by Gas Chromatography–Thermal Conductivity Detection

Analysis by GC/TCD showed that 22 of the 28 CK cylinders from HP Gas and 15 of the 16 cylinders from Custom Gas Solutions contained detectable levels of CCl₄. On the other hand, only 3 of the 28 CK cylinders from Semiconductor Resources showed a quantifiable signal for CCl₄ in the chromatogram.

This GC/TCD data provides an example of how the trends of these attribution signatures can be used. In these data sets, CCl4 was detected in about 78% of the CK cylinders from HP Gas, about 93% of the cylinders from Custom Gas Solutions, and only about 10% of the cylinders from Semiconductor Resources. Analysis of any single cylinder found to lack CCl4 would not unambiguously prove that it was procured from Semiconductor Resources; however, it would indicate that Semiconductor Resources was a likely source. Analyses of several cylinders that all showed the same trend would greatly increase the accuracy of that determination.

This trend was less defined by NMR, most likely because the CCl₄ peak in the NMR spectrum was on the downfield slope of the much larger and stronger CK peak; therefore, the CCl₄ peak was easily obscured by the CK peak.

3.2.2 Carbon Tetrachloride Concentration by Gas Chromatography–Thermal Conductivity Detection

While a lack of CCl4 identified in the GC/TCD chromatogram indicated Semiconductor Resources as a likely vendor source, a relatively high concentration of CCl4 provided additional information. An examination of the CCl4 concentrations in CK samples from HP Gas shows that, in the 15 analyses from 2011 through 2013, the highest concentration of CCl4 detected by GC/TCD was 0.6%. Of the 13 analyses done between 2005 and 2010, all but two showed concentrations of 0.9% or more, with an average of 3.8%.

Of the 15 CK cylinders from Custom Gas Solutions that were analyzed in which CCl₄ was detected (3 from 2009, 8 from 2010, and 4 from 2012), only 2 showed concentration levels higher than 1%. Not surprisingly, given that CCl₄ was detected in only 3 of the 28 cylinders from Semiconductor Resources, none of these cylinders showed CCl₄ concentration levels above 1%.

This suggests that a cylinder from an unknown commercial source that shows more than a 1% concentration level of CCl₄ may be an older cylinder from HP Gas. Therefore, this trend could represent a possible attribution signature, not only for a specific vendor but also to a time of production.

3.2.3 Water and Hydrogen Cyanide Identification by ¹H-NMR Spectroscopy

As mentioned in Section 2.2, ¹H-NMR spectra were collected for the majority of the CK analyses done by NMR, in the interest of recognizing additional impurities. CK contains no hydrogen; therefore, a sample of pure CK should reveal nothing in the ¹H-NMR spectrum. In addition, the common impurities (i.e., C₂N₂, CCl₄, and C₂Cl₄) that were observed during the analyses have no hydrogen. ¹H-NMR is able to detect compounds in the parts-per-million range, so impurities that were well under 0.1% levels in these samples could easily have been detected if they had contained hydrogen.

In most of the ¹H-NMR spectra, the strongest resonance detected came from H₂O, as confirmed by a simple spiking experiment. In all of the samples of CK cylinders from HP Gas for which ¹H-NMR spectra were collected, there were two strong and clear signals in the ¹H spectrum: H₂O and AC (this was also confirmed through spiking). If AC had been present in the sample at a concentration greater than about 0.1%, it would have been quantified in the ¹³C-NMR spectrum. Therefore, despite the clarity of the signals in the ¹H-NMR spectra, the actual concentrations were likely lower. Nonetheless, the presence of H₂O and AC as clear resonances in the ¹H-NMR spectrum was very consistent in the HP Gas samples.

Similar ¹H-NMR spectra were seen in only a few of the samples from each of the other two vendors, including two in which AC gave a stronger resonance signal than H₂O. A similar pattern in the CK ¹H-NMR spectra to that of CK from HP Gas was observed in 3 of the 11 cylinders from Custom Gas Solutions and 2 of the 19 cylinders from Semiconductor Resources. (It should be noted that the only sample for which AC was strong enough to be quantified in the ¹³C-NMR spectrum came from Semiconductor Resources.) For the majority of

the spectra from the other vendors, however, the H₂O signal was quite weak or broad, and the AC signal was often not seen at all.

Given the qualitative nature of the results from the ¹H-NMR spectra, a compilation of the ¹H-NMR spectra from samples from the different vendors is included in Figure 3. The top panel of that figure shows ¹H-NMR spectra of samples from HP Gas, and the following two panels show spectra of samples from Semiconductor Resources and Custom Gas Solutions. Each panel shows ¹H-NMR spectra offset from each other vertically and horizontally, for ease of viewing. In each panel, the spectra have been normalized relative to the intensity of the H₂O signal (2.17 ppm) and displayed in reverse chronological order from front to back. Note that the baselines in some of the spectra in the bottom two panels appear noisy, indicating that the H₂O resonance signals were very low, to such an extent that by normalizing the signal from H₂O, the baseline was over expanded.



Figure 3. Stacked ¹H-NMR spectra of CK samples from each of the three vendors, with most recent spectra in the front. Spectra were normalized to the H₂O resonance at 2.17 ppm: (top) HP Gas, (middle) Semiconductor Resources, and (bottom) Custom Gas Solutions.

ACRONYMS AND ABBREVIATIONS

hydrogen cyanide
ethylene tetrachloride
cyanogen
chemical attribution signature
carbon tetrachloride
phosgene
cyanogen chloride
carbon dioxide
U.S. Army Edgewood Chemical Biological Center
Forensic Analytical Center
gas chromatography
water
nuclear magnetic resonance
Protective Equipment Team
thermal conductivity detection

	Analysis	NMR data							GC/TCD data						
Manufacturer	date	NCCN	CCl4	C2Cl4	AC	unk	Info from ¹ H	N2/O2	CO2	NCCN	H2O	AC	CCl4	unk	
HP Gas, LLC	Aug-13	0.20				0.40	water & AC	0.05	1.51	1.57				0.02	
HP Gas, LLC	Jun-13	0.80					water & AC	0.04	0.60	2.32			0.04	0.02	
HP Gas, LLC	Jun-13	0.40					water & AC	0.01	1.32	1.28					
HP Gas, LLC	Jun-13	0.70		0.10			water & AC	0.02	1.05	2.02				0.02	
HP Gas, LLC	Apr-13	0.10					water & AC	0.01	0.03	0.07			0.11	0.02	
HP Gas, LLC	Oct-12	0.60		0.10			water & AC	0.02	0.34	1.55			0.36		
HP Gas, LLC	Oct-12	0.70	0.50	0.20			water & AC	0.02	2.39	2.04			0.45		
HP Gas, LLC	Oct-12	0.30	1.00	0.10			water & AC	0.01	0.46	1.37			0.22		
HP Gas, LLC	Sep-12	0.20	0.40	0.10			water & AC	0.02	0.80	0.72			0.46		
HP Gas, LLC	Sep-12	1.70					water & AC	0.01	0.28	2.49			0.01		
Custom Gas Solutions	Sep-12	0.50				0.30	broad water	0.02	0.08	1.01	0.01		0.11		
Custom Gas Solutions	Sep-12	No imp	ourities s	een by ¹	³ C-NM	R	broad water	0.02	0.06	0.31	0.01		0.13		
Custom Gas Solutions	Sep-12	0.80		0.20			broad water	0.02	2.70	2.56	0.01		0.06		
Custom Gas Solutions	Aug-12		0.30				broad water	0.01	0.02	0.08	0.00		0.29		
Semiconductor Resources	Feb-12	0.50					sharp water	0.70	0.30	0.80	0.30				
Semiconductor Resources	Feb-12	0.20					sharp water	0.80	1.20	1.20	0.20				
Semiconductor Resources	Nov-11	0.30		0.10			sharp water	1.30	1.70	1.00	0.30				
Semiconductor Resources	Nov-11	0.30		0.10			sharp water	1.10	0.10	0.70	0.20				
Semiconductor Resources	Nov-11	0.40	0.60	0.10			broad water	0.90	1.20	1.00	0.30				
Semiconductor Resources	Jun-11	No imp	ourities s	een by ¹	³ C-NM	R	sharp water	1.70	0.20	0.10	0.70				
Semiconductor Resources	Jun-11	0.30					sharp water, weak AC	1.90	0.05	0.50	0.70				
Semiconductor Resources	May-11	0.20					sharp water	2.10	0.02	0.60	0.40				
Semiconductor Resources	May-11	0.30					sharp water	2.00	0.02	0.20	0.40				
Semiconductor Resources	May-11	0.10					sharp water, weak AC	1.00	0.06	0.40	0.80	0.01			
HP Gas, LLC	Jan-11	0.50		trace			water & AC	0.80	0.04	0.50	0.20	0.07	0.10		
HP Gas, LLC	Jan-11	0.10					water & AC	0.80	0.04	0.30	0.30	0.03	0.05		
HP Gas, LLC	Jan-11	0.50		trace	trace		water & AC	1.20	0.09	1.10	0.50	0.10			
HP Gas, LLC	Jan-11	0.20		trace			water & AC	1.00	0.07	0.10	0.30	0.04	0.10		
HP Gas, LLC	Jan-11	0.40	0.30				water & AC	1.00	0.10	0.80	0.30	0.10	0.60		

APPENDIX A: Reverse Chronological Listing of Impurities Detected in Cyanogen Chloride Cylinders

	Analysis		NMR data							GC/TCD data						
Manufacturer	date	NCCN	CCl4	C2Cl4	AC	unk	Info from ¹ H	N2/O2	CO2	NCCN	H2O	AC	CCl4	unk		
HP Gas, LLC	Dec-10	1.70	4.60	0.20	trace		water & AC	0.80	0.20	3.60	0.40	0.10	2.70			
HP Gas, LLC	Dec-10	0.80		0.20			water & AC	0.60	0.04	0.90	0.70	0.09				
HP Gas, LLC	Nov-10	1.20	0.70				water & AC	0.90	0.20	3.20	0.80	0.08	1.00			
HP Gas, LLC	Nov-10	1.00	2.10				water & AC	0.70	0.06	1.80	0.20	0.10	1.50			
Semiconductor Resources	Sep-10	1.10		trace			broad water	0.90	0.40	2.30	0.70					
HP Gas, LLC	Sep-10	0.70	1.20	0.20			water & AC	0.80	0.40	1.70	0.30	0.05	0.90			
Semiconductor Resources	Aug-10	1.80		0.20			sharp water	0.60			0.20					
Semiconductor Resources	Aug-10	0.80		0.10			sharp water	0.80	0.20	0.80	0.30					
Semiconductor Resources	Aug-10	1.10		0.10			sharp water			1.20		0.10	0.20	0.10		
Custom Gas Solutions	Jul-10	No NM	R data v	vas coll	ected fo	r this s	ample			0.10			2.30	1.00		
Custom Gas Solutions	Apr-10	1.10					water & AC	0.30	0.03	0.60	0.90	0.10	0.02	0.01		
Custom Gas Solutions	Apr-10	0.60					water & AC	0.20	0.06	0.30	1.70	0.09	0.07			
Custom Gas Solutions	Apr-10		0.40				water & AC	0.40	0.01	0.01	1.20	0.04	2.60	0.02		
Semiconductor Resources	Mar-10	0.20					many peaks	0.60	0.02	0.60	0.50					
Semiconductor Resources	Mar-10	0.20					strong water & AC	0.50	0.01	0.40	0.40					
Semiconductor Resources	Mar-10	0.40					many peaks	0.60	0.01	0.50	0.30					
Semiconductor Resources	Mar-10	0.40					weak water, strong AC	0.40	0.01	0.40	0.40					
Semiconductor Resources	Mar-10	1.10					weak water, many peaks	0.90	0.20	0.70	0.50					
Custom Gas Solutions	Feb-10	0.20		small			water & small AC	0.80	0.03	0.30	0.50	0.02	0.10			
Custom Gas Solutions	Jan-10	0.60	0.70				water & small AC	1.10	0.10	0.30	0.50		1.00	0.03		
Custom Gas Solutions	Jan-10		1.20				AC & many other peaks	0.70	0.10	0.06	0.40		1.30	0.02		
Custom Gas Solutions	Jan-10	No imp	urities se	een by ¹	³ C-NM	R	water & others	0.90	0.06	0.30	0.30		0.20	0.02		
HP Gas, LLC	Dec-09	2.60	3.80				water & AC	0.90	0.70	2.80	0.30	0.06	6.00			
HP Gas, LLC	Dec-09	2.20	3.30				water & AC	0.80	0.03	1.20	0.20	0.10	4.90			

APPENDIX A: Reverse Chronological Listing of Impurities Detected in Cyanogen Chloride Cylinders

	Analysis			N	MR da	ta		GC/TCD data								
Manufacturer	date	NCCN	CCl4	C2Cl4	AC	unk	Info from ¹ H	N2/O2	CO2	NCCN	H2O	AC	CCl4	unk		
HP Gas, LLC	Oct-09	No NM	R data v	was coll	ected fo	r this sa	ample	0.40	0.20	1.10	2.10	0.10	0.90			
HP Gas, LLC	Oct-09	No NM	R data v	was coll	ected fo	r this sa	ample	0.60	0.40	1.50	2.00	0.10	2.10			
Semiconductor Resources	May-09	No NM	R data v	was coll	ected fo	r this sa	ample	0.77	0.15	0.64	0.38		0.05			
Semiconductor Resources	May-09	No NM	R data v	was coll	ected fo	r this sa	ample	0.95	1.77	0.52	0.09		0.13			
Custom Gas Solutions	Apr-09	No NM	R data v	was coll	ected fo	r this sa	ample	0.36	0.00	0.64	0.30					
Custom Gas Solutions	Apr-09	No NM	R data v	was coll	ected fo	r this sa	ample	0.34		0.12	0.12		0.19			
Custom Gas Solutions	Apr-09	No NM	R data v	was coll	ected fo	r this sa	ample	0.80	0.02	0.46	0.18		0.11			
Custom Gas Solutions	Apr-09	No NM	R data v	vas coll	ected fo	r this sa	ample	0.51	0.05	0.79	0.14		0.13			
Specialty Gases of America (Semiconductor Resources)	Nov-08	No NM	R data v	was coll	ected fo	r this sa	ample	N/A	N/A	2.60	0.03	0.26				
Specialty Gases of America (Semiconductor Resources)	Nov-08	No NM	No NMR data was collected for this sample								0.20	0.40				
Specialty Gases of America (Semiconductor Resources)	Oct-08			0.10	0.30		No ¹ H data	N/A	N/A	0.17		0.40				
Stillwater (HP Gas, LLC)	Sep-08	0.40	3.10				water & AC	N/A	N/A	3.80		0.20	6.60			
Specialty Gases of America (Semiconductor Resources)	Mar-06	No imp	urities s	een by ¹	³ C-NM	R	No ¹ H data	N/A	N/A	1.10						
Specialty Gases of America (Semiconductor Resources)	Oct-05	No imp	urities s	een by ¹	³ C-NM	R	No ¹ H data	N/A	N/A	0.10						
Specialty Gases of America (Semiconductor Resources)	Oct-05	No imp	urities s	een by ¹	³ C-NM	R	No ¹ H data	N/A	N/A	1.30						
Specialty Gases of America (Semiconductor Resources)	Oct-05	No imp	urities s	een by ¹	³ C-NM	R	No ¹ H data	N/A	N/A	0.30						
TL2 Gases (HP Gas, LLC)	Mar-05	No NM	No NMR data was collected for this sample										5.20			
TL2 Gases (HP Gas, LLC)	Feb-05	No NM	No NMR data was collected for this sample										10.10			
TL2 Gases (HP Gas, LLC)	Jan-05	4.10					water & AC	No imp	urities	were d	etecte	d by G	C/TCD			

APPENDIX A: Reverse Chronological Listing of Impurities Detected in Cyanogen Chloride Cylinders

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	Analysis			ſ	NMR dat	а		GC/TCD data							
Manufacturer	date	NCCN	CCI4	C2Cl4	AC	unk	Info from ¹ H	N2/O2	CO2	NCCN	H2O	AC	CCI4	unk	
HP Gas, LLC	Aug-13	0.20				0.40	water & AC	0.05	1.51	1.57				0.02	
HP Gas, LLC	Jun-13	0.80					water & AC	0.04	0.60	2.32			0.04	0.02	
HP Gas, LLC	Jun-13	0.40					water & AC	0.01	1.32	1.28					
HP Gas, LLC	Jun-13	0.70		0.10			water & AC	0.02	1.05	2.02				0.02	
HP Gas, LLC	Apr-13	0.10					water & AC	0.01	0.03	0.07			0.11	0.02	
HP Gas, LLC	Oct-12	0.60		0.10			water & AC	0.02	0.34	1.55			0.36		
HP Gas, LLC	Oct-12	0.70	0.50	0.20			water & AC	0.02	2.39	2.04			0.45		
HP Gas, LLC	Oct-12	0.30	1.00	0.10			water & AC	0.01	0.46	1.37			0.22		
HP Gas, LLC	Sep-12	0.20	0.40	0.10			water & AC	0.02	0.80	0.72			0.46		
HP Gas, LLC	Sep-12	1.70					water & AC	0.01	0.28	2.49			0.01		
HP Gas, LLC	Jan-11	0.50		trace			water & AC	0.80	0.04	0.50	0.20	0.07	0.10		
HP Gas, LLC	Jan-11	0.10					water & AC	0.80	0.04	0.30	0.30	0.03	0.05		
HP Gas, LLC	Jan-11	0.50		trace	trace		water & AC	1.20	0.09	1.10	0.50	0.10			
HP Gas, LLC	Jan-11	0.20		trace			water & AC	1.00	0.07	0.10	0.30	0.04	0.10		
HP Gas, LLC	Jan-11	0.40	0.30				water & AC	1.00	0.10	0.80	0.30	0.10	0.60		
HP Gas, LLC	Dec-10	1.70	4.60	0.20	trace		water & AC	0.80	0.20	3.60	0.40	0.10	2.70		
HP Gas, LLC	Dec-10	0.80		0.20			water & AC	0.60	0.04	0.90	0.70	0.09			
HP Gas, LLC	Nov-10	1.20	0.70				water & AC	0.90	0.20	3.20	0.80	0.08	1.00		
HP Gas, LLC	Nov-10	1.00	2.10				water & AC	0.70	0.06	1.80	0.20	0.10	1.50		
HP Gas, LLC	Sep-10	0.70	1.20	0.20			water & AC	0.80	0.40	1.70	0.30	0.05	0.90		
HP Gas, LLC	Dec-09	2.60	3.80				water & AC	0.90	0.70	2.80	0.30	0.06	6.00		
HP Gas, LLC	Dec-09	2.20	3.30				water & AC	0.80	0.03	1.20	0.20	0.10	4.90		
HP Gas, LLC	Oct-09	No NMF	R data wa	s collect	ted for th	nis samp	le	0.40	0.20	1.10	2.10	0.10	0.90		
HP Gas, LLC	Oct-09	No NMF	R data wa	s collect	ted for th	nis samp	le	0.60	0.40	1.50	2.00	0.10	2.10		
Stillwater (HP Gas, LLC)	Sep-08	0.40	3.10				water & AC	N/A	N/A	3.80		0.20	6.60		
TL2 Gases (HP Gas, LLC)	Mar-05	No NM	R data wa	s collect	ted for th	nis samp	le						5.20		
TL2 Gases (HP Gas, LLC)	Feb-05	No NM	R data wa	s collect	ted for th	nis samp	le						10.10		
TL2 Gases (HP Gas, LLC)	Jan-05	4.10					water & AC	No impu	urities v	were de	tected	by GC/	TCD		

APPENDIX B: Listing of Impurities Detected in Cyanogen Chloride Cylinders from HP Gas, LLC

	Analysis		NMR data						GC/TCD data						
Manufacturer	date	NCCN	CCl4	C2Cl4	AC	unk	Info from ¹ H	N2/O2	CO2	NCCN	H2O	AC	CCI4	unk	
Semiconductor Resources	Feb-12	0.50					sharp water	0.70	0.30	0.80	0.30				
Semiconductor Resources	Feb-12	0.20					sharp water	0.80	1.20	1.20	0.20				
Semiconductor Resources	Nov-11	0.30		0.10			sharp water	1.30	1.70	1.00	0.30				
Semiconductor Resources	Nov-11	0.30		0.10			sharp water	1.10	0.10	0.70	0.20				
Semiconductor Resources	Nov-11	0.40	0.60	0.10			broad water	0.90	1.20	1.00	0.30				
Semiconductor Resources	Jun-11	No impu	urities see	en by ¹³ C	-NMR		sharp water	1.70	0.20	0.10	0.70				
Semiconductor Resources	Jun-11	0.30					sharp water, weak AC	1.90	0.05	0.50	0.70				
Semiconductor Resources	May-11	0.20					sharp water	2.10	0.02	0.60	0.40				
Semiconductor Resources	May-11	0.30					sharp water	2.00	0.02	0.20	0.40				
Semiconductor Resources	May-11	0.10					sharp water, weak AC	1.00	0.06	0.40	0.80	0.01			
Semiconductor Resources	Sep-10	1.10		trace			broad water	0.90	0.40	2.30	0.70				
Semiconductor Resources	Aug-10	1.80		0.20			sharp water	0.60			0.20				
Semiconductor Resources	Aug-10	0.80		0.10			sharp water	0.80	0.20	0.80	0.30				
Semiconductor Resources	Aug-10	1.10		0.10			sharp water			1.20		0.10	0.20	0.10	
Semiconductor Resources	Mar-10	0.20					many peaks	0.60	0.02	0.60	0.50				
Semiconductor Resources	Mar-10	0.20					strong water & AC	0.50	0.01	0.40	0.40				
Semiconductor Resources	Mar-10	0.40					many peaks	0.60	0.01	0.50	0.30				
Semiconductor Resources	Mar-10	0.40					weak water, strong AC	0.40	0.01	0.40	0.40				
Semiconductor Resources	Mar-10	1.10					weak water, many peaks	0.90	0.20	0.70	0.50				
Semiconductor Resources	May-09	No NMF	R data wa	s collect	ed for th	nis samp	le	0.77	0.15	0.64	0.38		0.05		
Semiconductor Resources	May-09	No NMF	R data wa	s collect	ed for th	nis samp	le	0.95	1.77	0.52	0.09		0.13		
Specialty Gases of America (Semiconductor Resources)	Nov-08	No NMF	No NMR data was collected for this sample							2.60	0.03	0.26			
Specialty Gases of America (Semiconductor Resources)	Nov-08	No NMF	o NMR data was collected for this sample						N/A		0.20	0.40			

APPENDIX C: Listing of Impurities Detected in Cyanogen Chloride Cylinders from Semiconductor Resources

	Analysis			ſ	NMR dat	a		GC/TCD data								
Manufacturer	date	NCCN	CCl4	C2Cl4	AC	unk	Info from ¹ H	N2/O2	CO2	NCCN	H2O	AC	CCI4	unk		
Specialty Gases of America	Oct 08			0.10	0.20		No ¹ II doto	NI / A	NI/A	0 17		0.40				
(Semiconductor Resources)	000-08			0.10	0.30		No H data	N/A	NA	0.17		0.40				
Specialty Gases of America	Mar 06			an hu ¹³ 0			No ¹ II doto	NI / A	NI/A	1 10						
(Semiconductor Resources)	Ivial-00	No impi	urities see	en by C	-NIVIR		No H data	N/A	NA	1.10						
Specialty Gases of America	Oct 05			an hu ¹³ 0			No ¹ II doto	NI / A	NI/A	0 10						
(Semiconductor Resources)	000-05	No impi	unities see	en by C	-NIVIR		No H data	N/A	NA	0.10						
Specialty Gases of America	Oct OF			¹³ c			N. ¹ 11 1-4-	NI / A	NI / A	1 20						
(Semiconductor Resources)	000-05	NO IMPI	urities see	en by C	-NIVIR		No H data	N/A	N/A	1.50						
Specialty Gases of America	Oct 05			an hu ¹³			No ¹ II doto	NI/A		0.20						
(Semiconductor Resources)	000-05	NO IMPI	urities see	en by C	-NIVIR		No H data	N/A	N/A	0.50						

APPENDIX C: Listing of Impurities Detected in Cyanogen Chloride Cylinders from Semiconductor Resources

	Analysis		NMR data							GC/TCD data								
Manufacturer	date	NCCN	CCI4	C2Cl4	AC	unk	Info from ¹ H	N2/O2	CO2	NCCN	H2O	AC	CCl4	unk				
Custom Gas Solutions	Sep-12	0.50				0.30	broad water	0.02	0.08	1.01	0.01		0.11					
Custom Gas Solutions	Sep-12	No impu	urities see	en by ¹³ C	-NMR		broad water	0.02	0.06	0.31	0.01		0.13					
Custom Gas Solutions	Sep-12	0.80		0.20			broad water	0.02	2.70	2.56	0.01		0.06					
Custom Gas Solutions	Aug-12		0.30				broad water	0.01	0.02	0.08	0.00		0.29					
Custom Gas Solutions	Jul-10	No NMF	R data wa	s collect	ed for th	nis samp	le			0.10			2.30	1.00				
Custom Gas Solutions	Apr-10	1.10					water & AC	0.30	0.03	0.60	0.90	0.10	0.02	0.01				
Custom Gas Solutions	Apr-10	0.60					water & AC	0.20	0.06	0.30	1.70	0.09	0.07					
Custom Gas Solutions	Apr-10		0.40				water & AC	0.40	0.01	0.01	1.20	0.04	2.60	0.02				
Custom Gas Solutions	Feb-10	0.20		small			water & small AC	0.80	0.03	0.30	0.50	0.02	0.10					
Custom Gas Solutions	Jan-10	0.60	0.70				water & small AC	1.10	0.10	0.30	0.50		1.00	0.03				
Custom Gas Solutions	Jan-10		1.20				AC & many other peaks	0.70	0.10	0.06	0.40		1.30	0.02				
Custom Gas Solutions	Jan-10	No impi	urities see	en by ¹³ C	C-NMR		water & others	0.90	0.06	0.30	0.30		0.20	0.02				
Custom Gas Solutions	Apr-09	No NMF	No NMR data was collected for this sample						0.00	0.64	0.30							
Custom Gas Solutions	Apr-09	No NMR data was collected for this sample						0.34		0.12	0.12		0.19					
Custom Gas Solutions	Apr-09	No NMR data was collected for this sample						0.80	0.02	0.46	0.18		0.11					
Custom Gas Solutions	Apr-09	No NMF	R data wa	s collect	ed for th	nis samp	le	0.51	0.05	0.79	0.14		0.13					

APPENDIX D: Listing of Impurities Detected in Cyanogen Chloride Cylinders from Custom Gas Solutions

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